Development of High Capacity, High Safety, Ni-Based Cathode Materials for Lithium-Ion Batteries

S. Dalton, P. Onnerud, D. Novikov, J. Shi, J. Treger, R. Chamberlain, B. Barnett and C. Lampe-Onnerud*
TIAX LLC
Acorn Park, Cambridge, MA 02140, USA

Original equipment manufacturers (OEMs) of portable electronics, such as cellular phones and laptop computers, demand increased power density from lithium-ion batteries. Manufacturers of lithium-ion batteries have opportunities to meet these demands by incorporating higher energy density materials. Such is the motivation for transition from Co-based metal oxides to Ni-based metal oxides. One hurdle in this transition centers on safety performance, another critical concern of OEMs.

At TIAX, we have performed extensive evaluation of the thermal properties of metal oxide cathode materials. Our efforts have combined the use of thermal analysis techniques, including thermal gravimetric analysis (TGA), differential scanning calorimetry (DSC) and accelerating rate calorimetry (ARC), with detailed structural analysis using X-ray diffraction (XRD) and Rietveld refinements. Our studies have led us to identify key properties for consideration when assessing a materials safety potential for use in lithium-ion batteries. These properties relate to state-of-charge, atomic structure and powder properties.

Ni-based metal oxides, while providing increased capacity to >180 mAh/g, are known to exhibit higher reactivity in lithium-ion systems, particularly at elevated temperatures.[1] ARC data on commercially available $LiNiCoO_2$ confirm this increase in reactivity compared to $LiCoO_2$ [Fig. 1]. Interestingly, synthesis in our labs has shown that Ni-based materials can achieve thermal safety features similar to $LiCoO_2$. Figure 1 also includes ARC data for two TIAX synthesized Ni-based oxides. The TIAX Ni-containing materials show thermal properties much more similar to $LiCoO_2$ than $LiNiCoO_2$. These same TIAX synthesized materials also show the expected high capacity (>180 mAh/g) common among Ni-based materials.

An additional comparison was made using DSC and this is shown in Figure 2. Again, the total energy released on heating de-lithiated samples in the presence of electrolyte is similar between $LiCoO_2$ and the TIAX Ni-based materials.

Rietveld refinements of XRD patterns taken of these metal oxides help explain the mechanisms for performance. TIAX analysis of many different Co and Ni-based metal oxides using Rietveld refinements indicates that atom ordering may play a crucial role in the safety performance of these materials.

We will present safety analysis of multiple cathode samples available commercially, as well as some novel materials recently developed at TIAX.

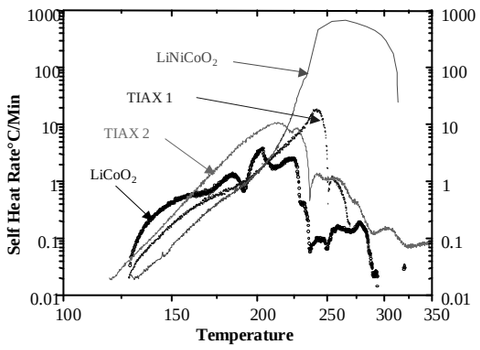

Figure 1. ARC analysis of four metal oxide samples charged to 4.2 V and tested in electrolyte (1M $LiPF_6$, 1:1 EC:DMC).

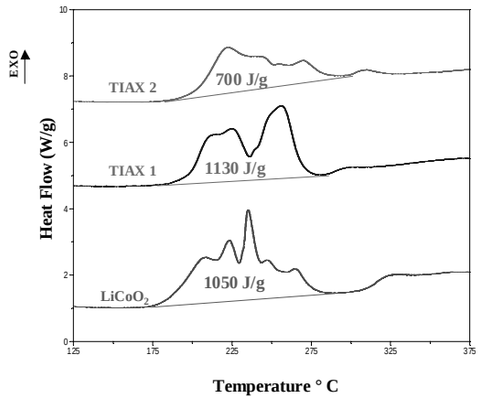

Figure 2. DSC analysis (5 °C/min to 400 °C) of 4 mg de-lithiated cathode material and 2 mg electrolyte (1 M $LiPF_6$, 1:1 EC:DMC).

[1] Ohzuku, T.; Yanagawa, T.; Kouguchi, M.; Ueda, A.; *J. Power Sources*, v.68, 131, 1997.